

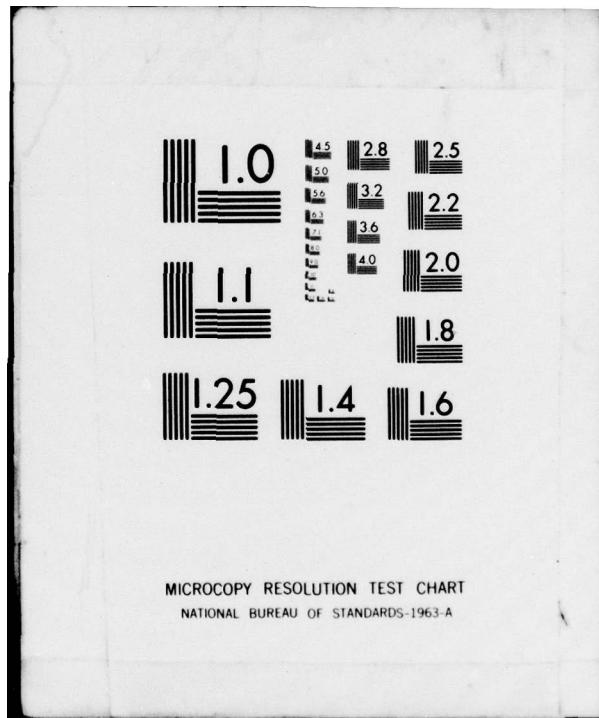
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How Plastics Fail -- The Churchill Conference

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Dr. W. D. Bascom

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3 August 1979

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br><br>This report reviews the presentations and discussion at the 5th International Conference on Deformation, Yield and Fracture of Polymers held at the University of Cambridge on 2-5 April, 1979. The work presented at the Conference gives some insight into the state-of-the-art of research on how polymeric materials fail. No breakthroughs were revealed, but the tone of the Conference suggested a coming to grips with nonlinear processes. |                       |   |

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## HOW PLASTICS FAIL—THE CHURCHILL CONFERENCE

The 4th International Conference on Deformation, Yield and Fracture of Polymers, held on 2-5 April 1979, is unofficially known as the "Churchill Conference" since it is regularly held at the Churchill College, Univ. of Cambridge. This Conference is sponsored by the Plastics and Rubber Institute and has been held every three years since 1970; this interval thought to be the gestation time for significant research results. The papers read at the Conference were largely from the UK and US, but among the attendees, there was good representation from Western Europe and Scandinavia.

The Churchill Conference has earned a reputation for heated discussion periods. Prof. Derek Hull (Univ. of Liverpool) suggested in his opening remarks that the battles be kept to mild skirmishes. He had no cause for concern because this year the Conference was rather subdued. Perhaps those people with, "special points of view," have expressed their opinions so often in past meetings that they felt no obligation to re-state them again.

**FRACTURE:** The first paper, given by Dr. C.G. Bragaw (E.I. duPont de Nemours, Wilmington, DE) should have brought a number of people to their feet when he challenged the validity of fracture mechanics for the design of polyethylene (PE) pipe. He first derived an expression relating the linear elastic fracture mechanics (LEFM) stress intensity factor and the crack tip radius. Then in testing PE he finds that the crack tip radius is quite variable so that the stress intensity factor cannot be a single valued failure criteria. Prof. J.G. Williams (Imperial College of Science and Technology, London) challenged Bragaw on his theoretical derivation pointing out that he was mixing LEFM with plasticity theory which invalidated his conclusions. Williams continued that a valid stress intensity factor could be attained under test conditions where the crack tip radius is essentially zero. Bragaw responded that such test conditions cannot be attained for PE.

Glassy polymers, such as polymethylmethacrylate (PMMA) or the cross-linked epoxys, are sufficiently brittle that their fracture behavior can be characterized by LEFM. One of the peculiarities of these polymers is that they will exhibit stable crack propagation under one set of conditions but unstable propagation under other conditions. Stable propagation is when the fracture proceeds by a steady advance of the crack as the load is increased. Unstable propagation is when the crack jumps forward spontaneously and then suddenly arrests due to the loss of stored elastic energy. Most workers believe that the yielding conditions at the crack tip determine whether stable or unstable fracture occurs. However, Prof. M.G. Phillips (Univ. of Bath) thinks otherwise. He asserts that upon the loss of excess elastic energy the normal and expected behavior is stable propagation and that arrest is caused by and coincides with a change in the material characteristics in the crack tip region.

In a study of the effect of methanol on the fracture of PMMA, he observes unstable cracking in the presence of the alcohol but cracking is stable in air. Using a high-speed recording technique, he finds that the crack actually slows down instead of coming to an abrupt halt as it should if arrest is caused by the stored elastic energy suddenly falling below a critical level. The crack slowing appears to occur as the methanol reaches the crack tip and alters the material properties. Phillips challenges the work on other glassy polymers, notably on epoxys (ESN 33-1:14), by stating that some agent, possibly water vapor, is responsible for crack arrest. The discussion indicated that his opponents were not convinced.

Dr. K.W. Thomson and Dr. B.W. Cherry (Monash Univ., Victoria, Australia) took the question of epoxy fracture from a state of confusion into complete chaos. They have measured the fracture energy of an epoxy polymer over four decades of strain rate (test machine crosshead speed) and observed several stable-unstable transitions between crosshead speeds of  $10^{-2}$  to  $10^2$  cm/min. which they attribute to an adiabatic-isothermal transition at low speeds (ca.  $10^{-1}$  cm/min) and to a relaxation transition of the polymer network at moderate speeds ( $10^{-1}$  to 10 cm/min). At cross-head speeds of less than  $10^{-1}$  cm/min they noted that the crack began to grow as the load was increased until some critical load was reached at which the fracture became unstable. This behavior is quite unusual for epoxy fracture and suggests that their material may have been atypical.

The subject of crack propagation instability was also the topic of a paper by Dr. R. Kambour (with Dr. S.A. Smith at General Electric Corporate Research and Development Laboratory, Schenectady, NY) who has been investigating the fracture of poly (2,6-methyl-1, 4-phenylene oxide, PM2PO) and its blends with polystyrene (PS). As for other thermoplastic polymers, PM2PO exhibits high toughness and stable crack propagation at low test rates but at about 10 cm/sec and higher, the fracture energy decreases and cracking is unstable. Kambour and Smith have shown that at low test rates failure involves both shear flow and craze formation at the crack tip. The crazes grow at small angles to the crack direction and as the crack front passes their growth terminates. At test rates of 10 cm/sec and unstable cracking, the amount of crazing is significantly reduced. Kambour suggested that at higher strain rates the ability of the polymer to shear flow is reduced. Crazing is less effected by strain rate but the overall reduction in crack tip plastic flow should result in a rise in stress concentration on the craze causing it to fail at a lower strain. The net result is a run-away process and crack growth instability. In the discussion of Kambour's paper, Dr. R.J. Young (Queen Mary College, Univ. of London) suggested that there is probably no fully general explanation for crack propagation instability. Kambour responded that it is nonetheless useful to look for generalities albeit limited.

Williams reported on some results on the notched impact behavior of PMMA and high density polyethylene (HDPE) at very high strain rates. In an earlier study of PMMA [*Int. J. Fracture*, 14 69 (1978)] he had

observed that at loading rates of less than 0.5 ms there was a sharp increase in impact strength of the order of a factor of two. In analysing these early results, Williams suggested that this effect was due to an abrupt increase in the yield strength of PMMA at high strain rates. Recently, Williams made similar impact tests on HDPE and again a sharp transition to high toughness at very high loading rates was observed. The curious aspect of these results was that the strain rate and temperature dependence of this transition were quite similar for both PMMA and HDPE. For such chemically dissimilar polymers this would not be expected if the phenomena were due to a molecular dependent property, e.g., yield strength. Williams examined the possibility that the sharp transient in impact strength was due to an isothermal-adiabatic (I-A) transition [I-A refers to the local heat generated at the crack tip by inelastic strain so that the polymer is heated to near its glass transition temperature ( $T_g$ ) or melting temperature ( $T_m$ )]. Earlier, Williams had discarded this explanation for the results with PMMA. To test the I-A transition hypothesis, Williams did a reverse calculation where he assumed that all the energy is converted into heat in the crack tip and raises the temperature in the tip to  $T_g$  or  $T_m$ . He then calculated the loading time at which this would occur. The value obtained for PMMA of 0.1 ms agrees reasonably with the experimental value of 0.1-0.2 ms. Moreover, the calculated temperature rise of 439°C agrees quite well with an experimental value reported in the literature some years ago. The calculated value of the transition loading rate for HDPE did not agree with the experimental result as well as it did for PMMA. The discrepancy for HDPE could be resolved by "recalculating" the HDPE fracture energy to take account of the difference in the crack tip stress distribution of the two polymers. Williams' paper produced a good bit of discussion. Dr. F.X. de Charentenay (Université de Technologie de Compiègne, France) asked about the effect of multiple strikes of the impact hammer because if there are multiple strikes it is impossible to get a unique strain energy. Williams answered that it is important only for the PMMA tests where it introduces scatter in the data. Dr. C.B. Buchnall (Cranfield Inst. of Technology) suggested that the calculations should include the heat of melting but Williams countered that he needed only to compute the time to reach  $T_m$  and not the melting of the entire plastic zone. Hull wanted to know if postfailure examination revealed any change in the surface morphology in going through the transition. Williams said there was too much deformation on the PE to detect any differences and that there were some features on the PMMA, but their meaning was unclear. Finally, Dr. R.W. Hertzberg (Lehigh Univ., Bethlehem, PA) asked about the sharpness of the notch and Williams made the interesting point that if the notch were very sharp, e.g. a natural crack, he thought one would not see the transition.

Dr. J.A. Manson (Lehigh Univ.) spoke on the fatigue crack propagation (FCP) response of impact modified nylon 66. The modifier is also a nylon of unspecified (proprietary) composition. He, along with Dr. M.D. Skibo (Sandia Laboratories, Calif.) and Hertzberg found that the additives markedly decrease the rate of FCP and in proportion to the amount of additives at low strain levels. This proportionality became

lost as the strain level was increased so that, considered overall, the material with 25% additive had optimum properties. At the high strain levels, the nylon 66 samples with 50-75% additive underwent gross heating which caused softening at the crack tip and thus the increase in FCP rate. It was also found that these nylon/nylon composites increase in FCP rate with increasing test frequency. This is the only polymer known where the fatigue rate increases with frequency, but Manson did not offer any explanation. Bucknall suggested that the hysteretic heating is a viscoelastic response of the molecules and may involve shear banding and crazing. Bucknall said that crack tip heating is enough to induce crystallinity which might explain the unusual increase in FCP rate with frequency. Manson agreed and stated further that the modifiers reduce the spherulite crystal size of the nylon 66.

The fatigue crack propagation in HDPE was the subject of a paper by deCharentenay (with Mr. F. Laghouati and Mr. J. Dewas, Université de Technologie de Compiègne, France) which they studied as a function of molecular weight (MW) and thermal history (quenching vs annealing). Lower FCP rates were obtained for quenched samples and for the higher MW material. De Charentenay attributed these results to a greater density of tie molecules between polymer crystallites; an explanation that has been given for the fatigue behavior of other polymers. Close examination of the crack tip processes revealed that for low MW material (<70,000) the process zone advanced continuously with fatigue cycling. On the other hand, the fatigue crack in the high MW polyethylene (>200,000) advances intermittently with each advance occurring after a number of fatigue cycles that depended on the test frequency. Microscopic evidence suggested that microvoiding was occurring in the process zone. Microvoiding at all frequencies is due to compressive stresses during crack closure. At low frequencies there is more time for plastic flow which cannot relax during compression.

In the paper by Dr. H.K. Kausch (Ecole Polytechnique Fédérale, Lausanne, Switzerland) he presented various arguments that the gradual disentanglement of polymer chains is the rate determining process in the yielding and fracture of glassy polymers below their  $T_g$ . He demonstrated a fracture specimen of PMMA where the fracture had been healed by pressing the two halves together and heating slightly above  $T_g$ . The region of separation disappeared completely and on retesting the same fracture energy was obtained as in the initial test. This result would not be possible if chain scission was governing the fracture process. Kausch also argued that the elastic energy release that would occur with chain scission would lead to such severe local yielding as to cause catastrophic failure under conditions where it is not observed experimentally.

Dr. G. Groeninckx (Catholic Univ., Leuven, Belgium) reported on an interesting polymer system, gelatin reinforced with polyethylacrylate latex particles. These materials are used as photographic emulsions and the latex particles serve to toughen the brittle gelatin. Groeninckx's

results demonstrate that the latex reduces the modulus and yield strength but increases the elongation at fracture. He concludes that shear yielding is the principal mode of deformation.

**YIELD:** Certainly crack propagation is an important aspect of polymer failure, but they can also fail by gross yielding, especially under static loads, i.e. stress relaxation. The stress relaxation of polymers was the subject of a paper by Dr. J.R. White (Univ. of Newcastle upon Tyne). He has treated analytically the problem of a molded bar which, because of the molding process, has a surface layer (skin) with a different relaxation behavior than the core. He found that the usual power law did not adequately describe this situation and has developed an alternate theory based on stress-aided thermal activation. Internal stresses were also included in the model. He found that by including a wide spectrum of relaxation times he could reproduce experimental trends, i.e., kinks in the relaxation curves, but has yet to obtain an analysis which gives a good fit to the experimental data.

Adiabatic instabilities can develop in the deformation of unnotched specimens as well as at notch tips. If the deformation is inhomogeneous, i.e., restricted to localized shear banding, and if a large part of the plastic work is converted into heat, catastrophic failure will ensue. Dr. J.D. Williams (with Dr. G. Mayer, North Carolina State Univ.) tested the torsional deformation of HDPE and polycarbonate (PC) at strain rates of  $10^{-3}$  to  $10 \text{ sec}^{-1}$ . They found inhomogeneous deformation occurs for HDPE at all testing rates and that at strain rates of  $5 \times 10^{-1} \text{ sec}^{-1}$  and higher there was clear evidence of adiabatic heating leading to localized plastic yielding. On the other hand, PC failed uniformly up to  $3 \times 10^{-2} \text{ sec}^{-1}$  but inhomogeneously at higher rates. Unlike HDPE, there was no evidence of the formation of local adiabatic instabilities.

Some polymers, such as polyvinylchloride (PVC), deform homogeneously until at some critical draw ratio, diamond shaped defects develop in the surface and with continued extension these defects grow in size and depth until they extend through to the other side. Curiously, they retain their diamond shape throughout the growth period. Such geometric regularity suggests a very specific deformation mechanism which has been the subject of studies by Dr. N. Walker, Dr. R.N. Haward and Dr. J. N. Hay (Univ. of Birmingham). Hay presented their most recent work in which they have printed a line grid on the surface of drawn PVC in order to observe the strain pattern around a diamond flaw as it grows. They observed that each grid element undergoes only a shear deformation in the draw direction. They were able to show why the deformation was so restricted from tests of the tensile stress-strain behavior of drawn PVC samples cut and tested at different angles ( $\theta$ ) to the draw direction. They found the yield strength to be lowest when  $\theta$  was  $0^\circ$ , i.e., the tensile stress is parallel to the draw direction. Moreover, the material undergoes strain hardening; as it begins to yield the stress must be increased for yielding to continue. At the tip of a growing diamond flaw (which always propagates normal to the draw direction) each element

undergoes shear yielding parallel to the draw direction but because of strain hardening it becomes energetically favorable for the next element to shear yield rather than for continued yielding of the previous element. Thus the diamond shape is preserved.

Dr. D.M. Shinozaki (Univ. of Manitoba) with Dr. C.M. Sargent (Univ. of Saskatchewan) have studied the stress-strain behavior of HDPE in terms of an inhomogeneous plastic flow model. The model assumes regions of varying hardness that deform in order of increasing hardness as the applied stress increases. The result is the buildup of internal stress that will affect the loading and unloading behavior. For example, a specimen loaded in tension begins to yield and narrow in diameter at some region along its length. On reversing the load, bulging occurs in the same location as the necking had occurred without the specimen necessarily reaching a compressive load. The authors performed a variety of tensile and compressive tests as well as various stress relaxation experiments and applied their model to the results. Their principal conclusion was that the total flow stress could be additively partitioned into two components; a rate dependent yield stress and an internal stress that is strain dependent but only weakly time dependent. They further concluded that the internal stress decays by molecular mechanisms distinct from the mechanism which governs the initial plastic deformation process.

The necking behavior of PE was also the subject of the paper by Dr. J.F. Jansson (with Mr. U.W. Gedde, Royal Institute of Technology, Stockholm) who has been studying the rather curious phenomena that if, after neck formation, the specimen is held under constant stress, there is a certain critical stress above which the neck fractures almost immediately. Below the critical stress, the neck is stable for considerable lengths of time. They have studied this effect for PE of different MW and at different temperatures and strain rates. They conclude that at high strain rates, large strains are concentrated in tie chains which favor fracture. At low strain rates, the material is able to relax so that local stresses are more easily distributed. The latter process is more effective in the high MW polymer.

Dr. B. Escaig (Université de Lille I, Lab Associe, au CNRS, Ville-neuve d'Ascq, France) presented a very interesting albeit controversial paper on a strictly thermodynamic analysis of polymer deformation below  $T_g$ . He obtained activation volumes ( $V_o$ ) for elastic and plastic deformation of PS and PMMA from stress relaxation data and showed that in stress-strain tests a definite yield stress can be associated with  $V_o$  reaching a near constant value. He took these critical yield stresses ( $\sigma_c$ ) as corresponding microstructural yield states which can be compared at different temperatures. Plots of the activation volume ( $V_o$ ) vs temperature indicate that below some critical temperature,  $T_c$ , the activation volume is essentially constant. The activation enthalpy ( $\Delta H_a$ ) was obtained from  $V_o$  and  $\sigma_c$  vs  $T$ . Plots of  $\Delta H_a$  vs  $T$  also show changes in slope at  $T_c$ . The activation free energies ( $\Delta G_a$ ) were obtained from  $\Delta H_a$  and

the entropy measured from dynamic tests (torsional pendulum). Plots of  $\Delta G_a$  vs T show strong inflection points at  $T_c$ . Escaig suggested that below  $T_c$ , deformation is insensitive to the free volume content, the energy barrier is essentially constant and the activation volume is quite small; of the order of one monomer unit. At temperatures higher than  $T_c$ , the deformation becomes dependent on free volume and the energy barrier is stress dependent. At these higher temperatures, Escaig concludes that molecular relaxations related to the  $\beta$  transition are involved.

Thermodynamic treatment of polymer deformation has always been controversial and Escaig's paper was the subject of much "cloakroom" discussion during the conference. The main issue is whether molecular interpretation of the results are justified. Many argue that inhomogeneities, either chemical or physical, control the deformation behavior rather than identifiable molecular entities. Escaig is not unaware of these questions and took great care in the synthesis and fabrication of the PS and PMMA specimens.

The fatigue behavior of polystyrene was the subject of a paper by Dr. J.A. Sauer (with Dr. S. Warty and Dr. S. Kaka, Rutgers Univ.) who argues that any mechanism which inhibits surface craze formation or breakdown will enhance fatigue lifetime. They showed that fatigue life increases as the MW of the PS was increased which is explained by an increase in the craze breakdown strength. Thin metal coatings on the PS specimen or running the tests in  $N_2$  gas enhanced fatigue life which Sauer said was due to the exclusion of  $O_2$  which by free radical attack causes craze breakdown. Finally, they showed that by immersing the polymer in polar liquids or by coating with an elastomer the fatigue life was enhanced. In these cases they suggested that surface flaw growth into crazes was inhibited by the liquid coating. To support this thesis, they showed that coating polished specimens had less of an effect than if the specimens were unpolished.

Dr. A.C. Smith reported on his work with Dr. B.J. Briscoe (Imperial College, Univ. of London) on the interfacial shear strength of polystyrene films. This is a continuation of the work by Briscoe in which the shear characteristics of the surface region of bulk polymer or of polymer films on glass substrates are determined by measuring the force required to move a smooth glass hemisphere slider over the surface. A normal force is applied to the slider. Although the interfacial shear behavior is closely related to the bulk yield properties, these tests are conducted under conditions not generally encountered in bulk testing, i.e., high hydrostatic stresses, high strain rates, low loading rates, and severe shear strains. In the work reported by Smith, films of polystyrene were cast from various solvents and tested at different temperatures. They concluded that the shear behavior depended primarily on the type of solvent used to cast the film and the amount of solvent retention. The tacticity (intermolecular orientation of the chains) had little effect on the results.

There is a certain amount of molecular chain scission during the yielding and rupture of polymers although how much this chain breakage contributes to yield strength and fracture energy is a matter of debate. Dr. D. Roylance (Mass. Institute of Technology) described the use of electron spin resonance (ESR) spectroscopy to detect the formation of free radicals resulting from chain scission. At present the technique is largely limited to studying fibers or films where the chains are aligned in the loading direction so as to maximize chain rupture. Roylance discussed the ESR methodology and some of the problems in interpreting the results of fiber rupture studies.

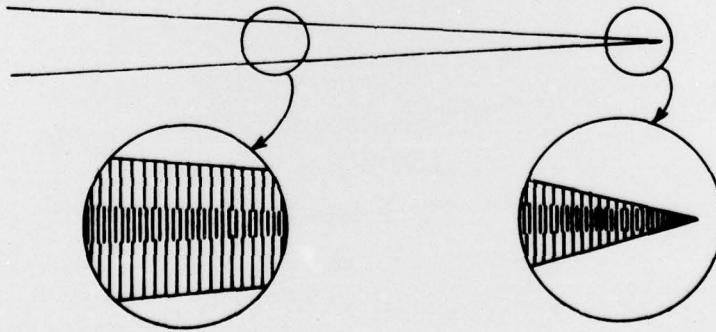
Hydrostatic pressure is known to strongly influence the mechanical properties of polymers and it is often suggested that the effect of pressure is formally equivalent to a lowering of the temperature, i.e., an increase in the mechanical relaxation times. R.A. Duckett and H. Summer (Univ. of Leeds) with Dr. S.H. Joseph (Imperial College, Univ. of London) and Dr. Z. Stachurski (Monash Univ., Clayton, Victoria, Australia) reported on the pressure dependence of the torsional yield and deformation of PVC. At 5-15°C above the  $T_g$ , hydrostatic pressure superimposed on the torsion test swept the effective  $T_g$  through the experimental temperature range changing the behavior from rubberlike to glassy. Their results showed a definite relation between shear yield stress and shear modulus but not the theoretically expected linear relation. These tests with PVC were done by enclosing the test rods in rubber sheaths to protect them from the pressurizing fluid (diester oil). Unprotected specimen exhibited crazes presumably induced by the fluid. However, existing theory does not allow for craze formation for torsional loads especially under hydrostatic pressure. The authors suggest a need for a fresh look at the theory of craze formation.

CRAZING: A few of the thermoplastic polymers exhibit a specific type of failure mechanism known as crazing. The mechanical stress creates a microvoid which, as it grows, develops ligaments of polymer across the cavity. The deformation of a polymer solely by craze formation is amenable to analysis because the unit of deformation, the craze, is discrete and its pertinent properties can be measured. Dr. Norman Brown (Univ. of Pennsylvania) has been determining the stress relaxation and stress-strain curves of glassy polymers and comparing the results with theoretical results calculated on the basis of crazing alone. He conducts these tests at low temperatures so as to suppress shear yielding in favor of crazing. In his presentation, Brown compared the measured strain in polychlorotrifluoroethylene with the strain computed from the density and size of the crazes. The agreement was generally good. In studies of the creep behavior of the same polymer, he assumed that the density and craze growth rate are constant. The results have the expected time-strain dependence. Stress relaxation behavior presents a more difficult problem because the craze length is a function of time. Brown assumed an exponential function for the time (in terms of stress) dependence of the craze length and also that the craze density is a function of the maximum stress. This analysis was tested for PS and good agreement

was obtained after the results were corrected for the shear yielding that occurred at the test temperature of 77K. Prediction of stress-strain curves presents an even more difficult problem since both craze density and craze length increase with time. Brown made the assumption that the change in craze length is an exponential function of stress and that the craze density is a linear function of strain. The computed curves correctly show the effect of strain rate but do not reproduce the sharp drop in stress after yielding begins. Brown suggested that the theory does not account for local changes in the stress level around the crazes.

Dr. H.R. Brown (Monash Univ., Victoria, Australia) has conducted a detailed study of the orientation of polymer chains in PS crazes using electron diffraction and optical birefringence. The diffraction study revealed the craze fibril matter to be highly oriented and with a draw ratio of about 6. Birefringence measurements on constant width crazes in specimens of varying thickness fit a model of fibrillated material of constant density with constant thickness skins of noncrazed material on either side.

As a craze grows in length, the span or thickness of the craze must also increase and the process can, in principle, occur either by drawing new polymer from the craze surface into the craze fibrils and maintaining the fibril extension rate ( $\lambda$ ) constant (surface drawing) or by increasing  $\lambda$  without drawing new material (fibril drawing). Dr. E.J. Kramer (with Dr. B.D. Lauterwasser, Cornell Univ.) discussed their transmission electron microscopy (TEM) study of the mechanism of craze growth in PS. They used the TEM to determine the fibril draw ratio and the stress at the craze surface. Films of PS were cast onto glass slides and then floated onto copper TEM grids that were stressed to produce crazes in the film. Two views of the craze as seen using TEM are given in the figure. There is a midrib of low density material that extends from the craze tip to the open end of the craze. Actually, the tip is filled



with the low density material; the more dense fibrils were not evident until about  $0.1 \mu\text{m}$  from the tip. Kramer and Lauterwasser found that the surface stress is constant along the length of the craze up to the tip where the stress increases slightly. They also determined that the density of the fibrils is constant along the craze length and slightly lower than the density of fibrils in the tip and along the midrib. They conclude that growth occurs by the surface drawing mechanism. In the craze tip the fibrils are drawn to a higher draw ratio than further back in the craze because of the higher stress in the tip.

Dr. N. Verheuln-Heymans (Université Libre de Bruxelles, Belgium) also concluded that craze thickening in PC occurs by surface drawing. She used a light reflection technique to determine that the craze strain is independent of craze length. She also pointed out that her results (and those of Kramer and Lauterwasser) put in doubt theories of crazing kinetics based on the tip growth being the rate determining factor. Both groups of workers determined that craze rupture occurs at the midrib and not by the  $\lambda$  of the fibrils increasing progressively toward the craze opening until ultimate strain is reached.

Dr. N.J. Mills (Univ. of Birmingham) has been analyzing some of the peculiar aspects of craze growth. For example, crazes growing on parallel but displaced planes will grow past each other without any deviation in their growth direction. In contrast, two parallel fatigue cracks deviate toward each other and eventually link up. Mills' analysis, one part of which treats the parallel crazes as a periodic array of edge dislocations, shows that crazes should pass each other without deviation so long as the ratio of the craze yield strength to the applied stress is greater than unity. Furthermore, the analysis shows that as the crazes pass each other there is a decline in the applied fracture energy indicating a slowing in the craze growth rate which is in fact observed. Another peculiarity of craze growth is that when a number of crazes initiate on a free surface under tensile loading, they grow to about the same length. (If they behaved like simple surface cracks, one craze would grow at the expense of the others.) This behavior is explained by the analysis which indicates that when the ratio of craze length to craze separation reaches 0.3 the applied fracture energy becomes constant.

**HIGHLY ORIENTED POLYMERS:** An especially active area of polymer research and development is the preparation and characterization of polymers extended to draw ratios of 10-30 and even higher. These materials have very high moduli and low gas permeability (ESN 33-7:283). The most widely studied of these highly drawn polymers is ultraoriented polyethylene (UOPE). However, despite its attractive properties, monofilaments of UOPE exhibit an irreversible creep under static loads. Dr. I. Ward and his associates (Univ. of Leeds) have been leaders in the development of UOPE and their work on its creep behavior was reported by Dr. M.A. Wilding. The extent of tensile creep and recovery is very MW dependent and Wilding and Ward examined filaments drawn from PE having low (100,000) and high (300,000) MWs. The creep and recovery of the low MW filaments

could be modeled by a simple spring and dash-pot assembly which included a single dash-pot with no restoring spring to model the unrecoverable strain. The creep of the high MW filaments could not be fit by this model at low strains which the authors explained by the need to reach a threshold stress before any nonrecoverable strain occurs. They suggest that two different deformation mechanisms are involved; the low MW creep is predominately a pull-out of crystallite chain folds whereas intercrystalline entanglements control the creep of the high MW filaments. To test these hypotheses they irradiated the low MW PE before drawing to create cross-links at the chain fold surfaces which would prevent chain pull-out. There was a decided improvement in the creep resistance and recovery behavior of the monofilaments drawn from the irradiated PE; their creep properties became equivalent to that of the high MW filaments. It was also shown that the introduction of a small amount (1.5/1000 C-atoms) of chain branching in the PE improves creep resistance; equivalent to the effect of irradiation.

A special type of oriented PE is obtained by stretching the bulk polymer to a modest draw ratio, about 7, and then annealing under pressure. This procedure develops large (about 0.2  $\mu\text{m}$ ) crystal lamella oriented along the draw direction and stacked perpendicular to their common c-axis. The resulting properties are not of any commercial interest but because of the large crystal size they are useful in studying the microdeformation mechanisms of oriented PE crystals. Dr. G.E. Attenburrow (with Dr. D.C. Bassett, Univ. of Reading) reported on their study of this moderately oriented PE. The elastic mechanical properties are quite similar to unoriented PE indicating that they are determined by the soft, amorphous interlamellar regions. In fracture tests, ductile yielding was observed under tensile loads along the draw direction but brittle failure occurred at angles of 20°-90° to the draw axis. Compressive tests and post-failure examination revealed the formation of kink banding by a uniform c-axis shear.

X-ray scattering studies of crystal orientation in drawn polymers was the subject of a paper by Dr. B. Heise (with Dr. H.G. Kilian and Dr. W. Wilke, Univ. of Ulm, FRG). They used both wide and small angle scattering. The overall intent of their work is to follow the progress of orientation as the draw ratio is increased. In their paper they reported on draw ratios up to two, and have developed a model where the cluster (crystallite) dimension changes by shear deformation parallel to the c-axis. The continuous decrease in crystal width is treated as a varying boundary condition. The theory is able to simulate the experimental results reasonably well for  $\lambda$  less than two. At higher values of  $\lambda$  they suggest that deformation by melting and recrystallization processes occurs for which their model cannot account.

Dr. R.S. Porter, at the University of Massachusetts heads another group active in ultraoriented polymers. With Dr. E.L. Thomas and Dr. E.S. Sherman (Univ. of Mass.) he has performed a microscopy study of the microstructure of UOPE. Using a number of electron microscopy tech-

niques, including dark field, nitric acid etching and gold decoration, they have established a hierarchy of crystal sizes. The predominate structures are fibrils 0.1-0.3  $\mu\text{m}$  in width and 0.03-0.1  $\mu\text{m}$  in thickness. These fibrils appear to be composed of microfibrils about 250 Å long. Dark field microscopy and gold decoration both indicated that the microfibrils were composed of an alternate sequence of amorphous and chain folded regions.

**COMPOSITES:** The mechanical properties of polymers, especially their stiffness and toughness, can be greatly enhanced by fibrous and particulate fillers. There were a number of papers on these composite materials at the Conference. Dr. F.J. Guild (Univ. of Bath) and Dr. D. Short (Plymouth Polytechnic) reported on the fracture of unidirectional glass fiber reinforced composites in four point bending. When the fibers are perpendicular to the long axis of the beam, fracture initiated on the tensile face and was catastrophic. When the fibers were parallel to the long axis of the beam, fracture again initiated on the tensile face but crack growth was slow until it reached the neutral axis at which point the beam split parallel to the neutral plane. The authors suggested that a correlation exists between a shape factor (area/perimeter<sup>2</sup>) and the onset of beam splitting.

Dr. G.J. Lake (Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford, UK) spoke about his work with Dr. R.F. Breidenback (Firestone Tire and Rubber Co., Akron, OH) on the tearing of rubber reinforced with steel cords. This material in steel belted automobile tires frequently fails by crack propagation in the rubber between the plies and the steel cord. Lake discussed the very high strain that can develop under rather modest loads along the edge of the composite near closely spaced cords in adjacent plies. These strains induce microcracks at the edge which coalesce into a single macroscopic crack. Using a two-ply model composite, Lake and Breidenback were able to simulate the interply failure observed in tires. They used a simple energy balance and were able to relate the growth rate of the macroscopic crack with the applied (cyclic) stress and showed that the behavior was close to that of the unreinforced rubber. They concluded that interply tearing was controlled solely by the properties of the rubber and not by the rubber/steel interface. Furthermore, they believe that their results show that despite differences in the mode of deformation an energetics approach to crack growth in rubber is as applicable to complex configurations as to simple sheet rubber test specimens.

Dr. J. Harding (Univ. of Oxford) reports on his work with Dr. T. Parry (Press Papers Ltd., London) on the compressive failure of composites. In the past, failure mechanisms based on the microbuckling of individual fibers have consistently overestimated the compressive strength of unidirectional composites. Various explanations have been offered for the discrepancy, one of them being that the fibers are not straight but tend to have a sinusoidal configuration. Certainly this would be the case for woven glass or graphite fiber laminates. Harding and Parry reformu-

lated the simple buckling theory to include matrix strains developed because of an undulating fiber configuration. They compared the calculated results with the experimental compressive failure stress of five commercial woven glass composites. The agreement was very good for stiff epoxy and polyester matrix materials but when the matrix was a low modulus polysiloxane resin they predicted a very low modulus, whereas the measured stiffness was much greater. Because their analyses was unable to predict the silicone laminate strength and also because the mode of failure was not always by well defined shear bands as their theory would predict, they question the general validity of their analysis.

Dr. D. Hull and Dr. M.J. Legg (Univ. of Liverpool) described their work on the effect of the properties of the matrix resin on properties of the composite. They used a series of chemically similar polyester resins which varied in modulus by a factor of two and in strain-to-failure by a factor of four. They tensile tested unidirectional laminates and pressurized axially wound pipes. Although they could get a correlation between resin toughness and transverse properties, the correlation with multiaxial loading was not conclusive.

The effect of absorbed water on the mechanical properties of glass and graphite composites has been a matter of much concern in recent years. This subject was dealt with directly in the presentation by Dr. L.J. Broutman (with Dr. R.H. Kim, Illinois Institute of Technology). The diffusion mechanisms of low MW solutes in polymers was the subject of a paper by Dr. A.H. Windle (Univ. of Cambridge) and the effect of imhomogeneities on solvent sorption was discussed by Dr. S.S. Sternstein (with Dr. J. Rosenthal and Dr. P. Herbert, Rensselaer Polytechnic Institute).

Broutman discussed the effect of low level stress and temperature on water absorption by graphite fiber, epoxy matrix composites. Both stressed and unstressed specimens were immersed in water at various temperatures. The stress was 25% of ultimate and at this low level there is no microcracking of the matrix. It was found that the applied stress accelerated the rate of water uptake near room temperature but at 60°C the rate is so fast in the unstressed samples that the effect of load is difficult to detect. The shear strength is degraded by adsorbed water, but applied stress during exposure had no effect except that it accelerates water uptake and thus the strength degradation. Broutman suggested two interpretations of the effect of applied stress on water absorption. One is that stress creates microscopic defects or interfacial separation which would enhance diffusion. Alternatively, the strain may create additional free volume in the resin.

The non-Fickian or, "case II", diffusion of liquids into polymers was the subject of the paper by Windle. This phenomenon occurs for many glassy polymers immersed in organic liquids at temperatures below the  $T_g$ . The liquid advances with a very sharp front between the fully swollen and unaffected polymer. Windle suggested that this process is governed by the molecular relaxation of the polymer subjected to the swelling

stress created by the diffusing liquid. He developed a simple expression for the rate of concentration of solute in a volume element at the diffusion front and the form of this equation implies a sharp boundary because the restraint of the unswollen glass on the swelling element severely limits the dimension of the element. His analysis predicts an induction time which agrees within a factor of two the observed induction time for the swelling of PMMA in methanol.

Sternstein discussed the important problem of the inhomogeneous swelling of polymers. Specifically, the swelling of polymers with non-uniform cross-link densities and/or fillers. He began by pointing out that since regions of different cross-link densities or a gradient in cross-linking around a filler particle will adsorb different amounts of solvent, internal stresses will develop which can effect the overall sorption characteristics of the polymer. Moreover, the inhomogeneous interactions of a solvent with a polymer cannot be described uniquely by the thermodynamic properties of the solvent and polymer. Even in the absence of a filler, there will still be localized fluctuations in cross-linked density. The swelling strain will be different in regions of low cross-linking compared to regions of excess cross-linking.

**SUMMARY:** The papers presented at the Churchill Conference do not by any means represent a complete coverage of research on polymer failure. Nonetheless, they do give an indication of the state of the art. Nothing especially novel was presented. Most of the papers described refinement or rethinking of past work. There may be breakthroughs in the understanding of the mechanisms of polymer failure in the future but the tone of the Conference suggests a maturing of this area of polymer science and a coming to grips with the difficult, nonlinear processes that determine how plastics fail.

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